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FLUORIDE GLASSES FROM SOL GELS

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The use of sol-gel coatings to strengthen oxide glasses has been demonstrated for the case of fused silica. Increases in strength to as much as 2.2 times the strength of uncoated glass have been obtained. The strengthening does not involve the annealing of surface microcracks, but rather the filling-in of such flaws. The strengthening does not depend on coating thickness over the range 2000-10000Å, but does depend significantly upon the state of hydrolysis of the substrate surface.

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FINAL REPORT

ON

FLUORIDE GLASSES FROM SOL GELS

submitted to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

by

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(AFOSR-85-0325)

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Professor D.R. Uhlmann

September 15, 1986

... ..., directed to the synthesis and crystallization behavior of fluoride glasses, was initiated in September, 1985. During the initial year, attention has been directed to both areas of the originally-proposed program. The research was carried out by Michele Andersen, a graduate student in the Department of Materials Science and Engineering, working under the technical supervision of Professor Uhlmann. Miss Andersen received her undergraduate degree in chemistry from MIT, and is well suited for carrying out the present research program with its strong emphasis on chemistry + materials.

In the part of the investigation dealing with the synthesis of fluoride glasses by sol-gel techniques, the system zirconium/barium lanthanum/aluminum has been selected as the starting point for the synthesis work. Single-component gels are known which were produced using zirconium and aluminum alkoxides; barium (like other alkaline earth) compounds have problems with solubility and/or miscibility; and relatively little is known about the behavior of lanthanum alkoxides.

In the present work, attention has been focussed on the synthesis of double alkoxides for use in ... ... to produce the desired oxide gels. The syntheses on which the work has begun are the following:

A. Lanthanum chloride + ... aluminum isopropoxide to produce the double alkoxide, lanthanum aluminum isopropoxide. That is: $LaCl_3 + 3KAl(O_iP_r)_4 \rightarrow La[Al(O_iP_r)_4]_3 + 3KCl$

... indicate that this synthetic route is effective

... of the double alkoxide, even without using a

... FTIR and NMR characterization should provide the desired

confirmation.

B. Barium isopropoxide + aluminum isopropoxide to produce the double alkoxide, barium aluminum isopropoxide. That is:

$$Ba(OiPr)_2 + 2Al(OiPr)_3 \rightarrow Ba[Al(OiPr)_4]_2$$
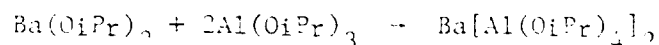
This synthesis is being carried out using $HgCl_2$ as a catalyst. Preliminary results are encouraging; but again, confirmation must await characterization by FTIR and NMR. In this case, successful prior synthesis using the route employed here was reported by Bradley and his co-workers.

C. Barium isopropoxide + zirconium isopropoxide to yield the double alkoxide, barium zirconium isopropoxide. That is:

$$Ba(OiPr)_2 + 2Al(OiPr)_3 \rightarrow Ba[Zr_3(OiPr)_{14}]$$
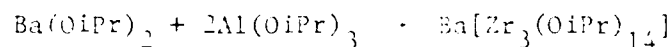
As with the barium aluminum isopropoxide, this synthesis is carried out using $HgCl_2$ as a catalyst. Work on this synthesis has only recently been initiated; but prior use of the approach by Bradley and his co-workers leads confidence that it will be successful.

D. Zirconium isopropoxide + aluminum isopropoxide to yield the double alkoxide, zirconium aluminum isopropoxide. That is:

$$Zr(OiPr)_2 + Al(OiPr)_3 \rightarrow \ldots$$
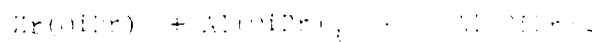
... is synthesis has only recently been initiated; and the
... ... has not been determined. The initial work
is being carried out in isopropanol.

E. Lanthanum isopropoxide + zirconium isopropoxide to yield the double alkoxide, lanthanum zirconium isopropoxide. That is:

$$La(OiPr)_3 + 3Zr(OiPr)_4 \rightarrow LaZr_3(OiPr)_{15}$$
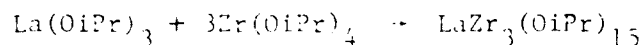
This synthesis has only recently been decided upon. Experimental work in this system should begin within the next month.

It is apparent that limitations exist in the ratios of the metal cations in these double alkoxides. They do, however, represent a useful starting point for testing the concept; and the PI team are confident that methods can be developed for increasing the flexibility in tailoring composition.

Work has also been initiated to explore the characteristics of fluoridation, and particularly the effects of fluoridation treatments on microstructure. In this work, gels are being prepared from zirconium isopropoxide, and will shortly be prepared from the double alkoxide, barium aluminum isopropoxide (the product of synthesis ... ... These gels will be exposed to trichlorofluoro methane, dichloro difluoro methane and methane under a range of conditions; and the resulting materials will be characterized extensively with respect to both chemistry and structure. This work will provide initial insight into the process of fluoridation, and should yield important input to designing the conditions for fluoridation of the candidate glass-forming compositions.

[...] carried out to date has been concerned with [...] double alkoxides based on the isopropoxide moiety. [...] the rates of hydrolysis are determined for the respective double alkoxides, preliminary partial hydrolysis of the slower-hydrolyzing species (or different degrees of partial hydrolysis for the two slower-hydrolyzing species) will be effected before adding the faster-(fastest-) hydrolyzing alkoxide solution. Should this approach not yield sufficiently homogeneous gels, new double alkoxides will be synthesized which contain alkoxy groups other than the isopropoxide so that the rates of hydrolysis of the different alkoxides can be substantially equalized.

In the second part of the investigation, attention is being directed to modeling the development of crystallinity in a body subject to a three-stage thermal history (cooling to the glassy state, reheating to a drawing temperature, and cooling again to form the glassy fiber). In the model, the two cooling rates and the heating rate + draw temperature are taken as arbitrary. The model is based on the analysis of crystallization statistics, which describes the number and size distribution of crystallites in a body which is subject to a given thermal history. This model has been used with success to describe the crystallization which takes place on reheating a glass as a function of the barrier to crystal nucleation (the crystal-liquid surface free energy).

To describe crystallization during the three-state thermal history of concern in the present work, modification of the existing

... ... undertaken to include second-stage cooling ... ... from the initially-cooled glassy state. Crystallization which takes place during the reheat stage has been found to depend upon the percent of crystallinity in the initially-formed glass, at least for volume fractions of crystallinity which exceed about 10^{-10}. That is, the degree of crystallinity in the as-formed glass affects the stability of the liquid against crystallization during subsequent heating above the glass transition temperature, save when the percent crystallinity in the as-formed glass is very small. These results suggest that very rapid cooling to form the initial glass-employing cooling rates which well exceed the minimum cooling rates for glass formation - well be advantageous for enhancing the resistance to crystallization on subsequent reheating.

As indicated above, modification of the computer code to describe three-stage cooling-reheating-recooling cycles is presently underway. Preliminary results have indicated the importance of the draw temperature and the temperature intervals among the draw temperature, liquidus temperature and glass transition temperature in affecting the degree of crystallization which will occur in the finally-cooled glass bodies (fibers in the case of present interest).

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